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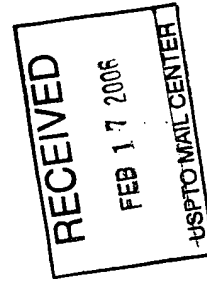
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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/751,164	12/31/2003	Gary F. Dandreaux	C-477	1558

7590 02/09/2006
Sun Chemical Corporation
222 Bridge Plaza South
Fort Lee, NJ 07024



EXAMINER

SHOSHO, CALLIE E

ART UNIT PAPER NUMBER

1714

DATE MAILED: 02/09/2006

Please find below and/or attached an Office communication concerning this application or proceeding.

Office Action Summary

Application No.

10/751,164

Applicant(s)

DANDREAU ET AL.

Examiner

Callie E. Shosho

Art Unit

1714

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

- 1) ☐ Responsive to communication(s) filed on ____.
- 2a) ☐ This action is **FINAL**. 2b) ☒ This action is non-final.
- 3) ☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

- 4) ☒ Claim(s) 1-20 is/are pending in the application.
- 4a) Of the above claim(s) ____ is/are withdrawn from consideration.
- 5) ☐ Claim(s) ____ is/are allowed.
- 6) ☒ Claim(s) 1-20 is/are rejected.
- 7) ☐ Claim(s) ____ is/are objected to.
- 8) ☐ Claim(s) ____ are subject to restriction and/or election requirement.

Application Papers

- 9) ☐ The specification is objected to by the Examiner.
- 10) ☐ The drawing(s) filed on ____ is/are: a) ☐ accepted or b) ☐ objected to by the Examiner.
Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).
Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).
- 11) ☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

- 12) ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).
- a) ☐ All b) ☐ Some * c) ☐ None of:
- ☐ Certified copies of the priority documents have been received.
 - ☐ Certified copies of the priority documents have been received in Application No. ____.
 - ☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

- | | |
|--|---|
| 1) <input checked="" type="checkbox"/> Notice of References Cited (PTO-892) | 4) <input type="checkbox"/> Interview Summary (PTO-413)
Paper No(s)/Mail Date. ____. |
| 2) <input type="checkbox"/> Notice of Draftsperson's Patent Drawing Review (PTO-948) | 5) <input type="checkbox"/> Notice of Informal Patent Application (PTO-152) |
| 3) <input checked="" type="checkbox"/> Information Disclosure Statement(s) (PTO-1449 or PTO/SB/08)
Paper No(s)/Mail Date <u>3/10/04 & 4/11/05</u> . | 6) <input type="checkbox"/> Other: ____. |

DETAILED ACTION

Claim Objections

1. Claims 5, 9, 16, and 18 are objected to under 37 CFR 1.75(c), as being of improper dependent form for failing to further limit the subject matter of a previous claim. Applicant is required to cancel the claim(s), or amend the claim(s) to place the claim(s) in proper dependent form, or rewrite the claim(s) in independent form.

Claim 5, which depends on claim 1, recites that the rosin-based resin is “about 0 wt% to about 40 wt.%” while claim 1 recites that the composition comprises rosin-based resin. Thus, claim 5, fails to further limit the scope of the claim on which it depends, namely, claim 1, given that the rosin-based resin is optional in claim 5 but required in claim 1. That is, claim 5 is broader than claim 1 given that while claim 1 requires the use of rosin-based resin such rosin-based resin is not required in claim 5 in light of the disclosure in claim 5 that the rosin-based resin is present in amount of 0 wt.%.

Similar objections are made with respect to claims 9, 16, and 18 which each depend on claim 1 and which the use of 0 wt.% alcohol solvent, 0 wt.% plasticizer, and 0 wt.% latex emulsion, respectively, while claim 1 requires the presence of alcohol solvent, plasticizer, and latex emulsion.

2. Claims 5-7, 9, 14, 16, and 18 objected to because of the following informalities:

Words appear to be missing in each of claim 5-7, 9, 14, 16, and 18 regarding what the wt.% of each claim refers to. It is suggested in claim 5, for instance, after “rosin-based resin”, the

phrase “is present in an amount of” is inserted or after 40 wt.%, the phrase “of the composition” is inserted. Similar suggestion is made in claims 6-7, 14, 16, and 18.

Claim Rejections - 35 USC § 112

3. The following is a quotation of the second paragraph of 35 U.S.C. 112:

The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the applicant regards as his invention.

4. Claims 3, 5, 9, and 16-18 are rejected under 35 U.S.C. 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention.

(a) Claim 3 recites an improper Markush group. In line 3, after “hydrocarbon-”, it is suggested that “and/or” is deleted and “and” is inserted.

(b) Claim 5, which depends on claim 1, recites that the rosin-based resin is “about 0 wt% to about 40 wt.%” while claim 1 recites that the composition comprises rosin-based resin. Thus, the scope of claim 5 is confusing because it is not clear how rosin-based resin can be required in claim 1 but be optional in claim 5, i.e. 0 wt.%. Clarification is requested.

Similar questions arise with respect to claims 9, 16, and 18 which each depend on claim 1 and which require the use of 0 wt.% alcohol solvent, 0 wt.% plasticizer, and 0 wt.% latex emulsion, respectively, while claim 1 requires the presence of alcohol solvent, plasticizer, and latex emulsion.

(c) Claim 17 recites that the thermoplastic latex emulsion is “modified” acrylics, “modified” methacrylics, etc. The scope of the claim is confusing because it is not clear what is meant by “modified” or what types of acrylics, methacrylics, etc. this encompasses.

(d) Claims 17 and 18, which each depend on claim 1, each recite the limitation “the thermoplastic latex emulsion” in line 1. There is insufficient antecedent basis for this limitation in the claim given that there is no disclosure of “thermoplastic latex emulsion” in claim 1. It is suggested that either “thermoplastic” is inserted before “latex emulsion” in claim 1 or “thermoplastic” is deleted from each of claims 17 and 18.

Claim Rejections - 35 USC § 102

5. The following is a quotation of the appropriate paragraphs of 35 U.S.C. 102 that form the basis for the rejections under this section made in this Office action:

A person shall be entitled to a patent unless –

(b) the invention was patented or described in a printed publication in this or a foreign country or in public use or on sale in this country, more than one year prior to the date of application for patent in the United States.

(e) the invention was described in (1) an application for patent, published under section 122(b), by another filed in the United States before the invention by the applicant for patent or (2) a patent granted on an application for patent by another filed in the United States before the invention by the applicant for patent, except that an international application filed under the treaty defined in section 351(a) shall have the effects for purposes of this subsection of an application filed in the United States only if the international application designated the United States and was published under Article 21(2) of such treaty in the English language.

6. Claims 1, 5-13, and 15-20 are rejected under 35 U.S.C. 102(e) as being anticipated by Hayashi et al. (U.S. 6,699,312).

Hayashi et al. disclose ink comprising 3-10% pigment, 0.1-10% fatty acid ester, i.e. plasticizer, 1-20% rosin, 1-20% glycol, i.e. alcohol solvent, styrene-acrylic emulsion, and

polyethyleneimine, i.e. acid neutralizing agent (col.4, lines 35-36, col.4, line 56-col.5, line 11, col.5, lines 26 and 33-36, col.6, line 56-col.7, line 1, and col.7, lines 14-20 and 33).

While there is no disclosure that the ink is a water-washable lithographic composition as presently claimed, applicants attention is drawn to MPEP 2111.02 which states that “if the body of a claim fully and intrinsically sets forth all the limitations of the claimed invention, and the preamble merely states, for example, the purpose or intended use of the invention, rather than any distinct definition of any of the claimed invention’s limitations, then the preamble is not considered a limitation and is of no significance to claim construction”. Further, MPEP 2111.02 states that statements in the preamble reciting the purpose or intended use of the claimed invention must be evaluated to determine whether the purpose or intended use results in a structural difference between the claimed invention and the prior art. Only if such structural difference exists, does the recitation serve to limit the claim. If the prior art structure is capable of performing the intended use, then it meets the claim.

It is the examiner’s position that the preamble does not state any distinct definition of any of the claimed invention’s limitations and further that the purpose or intended use, i.e. water-washable lithographic composition, recited in the present claims does not result in a structural difference between the presently claimed invention and the prior art ink and further that the prior art structure which is ink identical to presently claimed water-washable lithographic composition is capable of performing the recited purpose or intended use.

In light of the above, it is clear that Hayashi et al. anticipate the present claims.

7. Claims 1, 3-6, 8-10, 12-13, 15-16, 18, and 20 are rejected under 35 U.S.C. 102(b) as being anticipated by Krishnan et al. '022 (U.S. 6,444,022) taken in view of the evidence given in *Hawley's Condensed Chemical Dictionary*

Attention is drawn to example 2 of Krishnan et al. '022 that disclose lithographic composition comprising (i) 60% carbon black base comprising 40% carbon black, 20% rosin ester, and 3% monoethanol amine, (ii) 20% modified linseed oil comprising 27.94% polyethylene glycol and 16.2% phthalic anhydride, (iii) 25% latex, and (iv) 2% monoethanolamine. From this example, it is calculated that the ink comprises approximately 24% carbon black, 12% rosin ester, 3.8% monoethanolamine, 5.6% polyethylene glycol, 3.24% phthalic anhydride, and 25% latex. It is well known, as evidenced by *Hawley's Condensed Chemical Dictionary* (pages 878-879), that phthalic anhydride functions as a plasticizer. It is also disclosed that the rosin also includes maleic anhydride rosin or rosin salt. It is further disclosed that the ink is used in dry lithography (col.1, lines 5-6, col.3, lines 63-65, and col.4, lines 10 and 31-39). Given that Krishnan et al. '022 disclose composition identical to that presently claimed, it is clear that the composition would inherently be water-washable.

While there is no disclosure that the ink is a "wet" lithographic printing ink as presently claimed, applicants attention is drawn to MPEP 2111.02 which states that "if the body of a claim fully and intrinsically sets forth all the limitations of the claimed invention, and the preamble merely states, for example, the purpose or intended use of the invention, rather than any distinct definition of any of the claimed invention's limitations, then the preamble is not considered a limitation and is of no significance to claim construction". Further, MPEP 2111.02 states that statements in the preamble reciting the purpose or intended use of the claimed invention must be

Art Unit: 1714

evaluated to determine whether the purpose or intended use results in a structural difference between the claimed invention and the prior art. Only if such structural difference exists, does the recitation serve to limit the claim. If the prior art structure is capable of performing the intended use, then it meets the claim.

It is the examiner's position that the preamble does not state any distinct definition of any of the claimed invention's limitations and further that the purpose or intended use, i.e. "wet" lithographic printing ink, recited in the present claims does not result in a structural difference between the presently claimed invention and the prior art ink and further that the prior art structure which is ink identical to that presently claimed is capable of performing the recited purpose or intended use.

In light of the above, it is clear that Krishnan et al. '022 anticipate the present claims.

Claim Rejections - 35 USC § 103

8. The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

(a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negated by the manner in which the invention was made.

The factual inquiries set forth in *Graham v. John Deere Co.*, 383 U.S. 1, 148 USPQ 459 (1966), that are applied for establishing a background for determining obviousness under 35 U.S.C. 103(a) are summarized as follows:

1. Determining the scope and contents of the prior art.
2. Ascertaining the differences between the prior art and the claims at issue.

3. Resolving the level of ordinary skill in the pertinent art.
 4. Considering objective evidence present in the application indicating obviousness or nonobviousness.
9. This application currently names joint inventors. In considering patentability of the claims under 35 U.S.C. 103(a), the examiner presumes that the subject matter of the various claims was commonly owned at the time any inventions covered therein were made absent any evidence to the contrary. Applicant is advised of the obligation under 37 CFR 1.56 to point out the inventor and invention dates of each claim that was not commonly owned at the time a later invention was made in order for the examiner to consider the applicability of 35 U.S.C. 103(c) and potential 35 U.S.C. 102(e), (f) or (g) prior art under 35 U.S.C. 103(a).
10. Claims 3-4 are rejected under 35 U.S.C. 103(a) as being unpatentable over Hayashi et al. (U.S. 6,999,312) in view of Asada (U.S. 5,800,599).

The disclosure with respect to Hayashi et al. in paragraph 6 above is incorporated here by reference.

The difference between Hayashi et al. and the present claimed invention is the requirement in the claims of specific type of rosin.

Asada, which is drawn to inks, disclose the use of polymerized rosin and rosin modified phenol in order to prevent pigment present in the ink from becoming aggregated (col.2, lines 40-47).

In light of the motivation for using specific type of rosin disclosed by Asada as described above, it therefore would have been obvious to one of ordinary skill in the art to use such rosin

in the ink of Hayashi et al. in order to prevent pigment in the ink from aggregating, and thereby arrive at the claimed invention.

11. Claim 7 is rejected under 35 U.S.C. 103(a) as being unpatentable over Krishnan et al. (U.S. 6,444,022).

The disclosure with respect to Krishnan et al. '022 in paragraph 7 above is incorporated here by reference.

The difference between Krishnan et al. '022 and the present claimed invention is the requirement in the claim of the amount of rosin-based resin.

Krishnan et al. '022 disclose the use of 12% rosin-based resin, while the present claims require about 15% rosin-based resin.

It is apparent, however, that the instantly claimed amount of rosin-based resin and that taught by Krishnan et al. '022 are so close to each other that the fact pattern is similar to the one in *In re Woodruff*, 919 F.2d 1575, USPQ2d 1934 (Fed. Cir. 1990) or *Titanium Metals Corp. of America v. Banner*, 778 F.2d 775, 227 USPQ 773 (Fed.Cir. 1985) where despite a "slight" difference in the ranges the court held that such a difference did not "render the claims patentable" or, alternatively, that "a prima facie case of obviousness exists where the claimed ranges and prior art ranges do not overlap but are close enough so that one skilled in the art would have expected them to have the same properties".

In light of the case law cited above and given that there is only a "slight" difference between the amount of rosin-based resin disclosed by Krishnan et al. '022 and the amount disclosed in the present claims, it therefore would have been obvious to one of ordinary skill in

the art that the amount of rosin-based resin disclosed in the present claims is but an obvious variant of the amount disclosed in Krishnan et al. '022, and thereby one of ordinary skill in the art would have arrived at the claimed invention.

12. Claim 14 is rejected under 35 U.S.C. 103(a) as being unpatentable over Krishnan et al. '022 (U.S. 6,444,022).

The disclosure with respect to Krishnan et al. '022 in paragraph 7 above is incorporated here by reference.

The difference between Krishnan et al. '022 and the present claimed invention is the requirement in the claim of the amount of acid neutralizing agent, i.e. monoethanolamine.

Krishnan et al. '022 disclose the use of 3.8% monoethanolamine, while the present claims require about 5% monoethanolamine.

It is apparent, however, that the instantly claimed amount of monoethanolamine and that taught by Krishnan et al. '022 are so close to each other that the fact pattern is similar to the one in *In re Woodruff*, 919 F.2d 1575, USPQ2d 1934 (Fed. Cir. 1990) or *Titanium Metals Corp. of America v. Banner*, 778 F.2d 775, 227 USPQ 773 (Fed.Cir. 1985) where despite a "slight" difference in the ranges the court held that such a difference did not "render the claims patentable" or, alternatively, that "a prima facie case of obviousness exists where the claimed ranges and prior art ranges do not overlap but are close enough so that one skilled in the art would have expected them to have the same properties".

In light of the case law cited above and given that there is only a "slight" difference between the amount of monoethanolamine disclosed by Krishnan et al. '022 and the amount

disclosed in the present claims, it therefore would have been obvious to one of ordinary skill in the art that the amount of monoethanolamine disclosed in the present claims is but an obvious variant of the amount disclosed in Krishnan et al. '022, and thereby one of ordinary skill in the art would have arrived at the claimed invention.

13. Claims 1 and 3-20 are rejected under 35 U.S.C. 103(a) as being unpatentable over Krishnan et al. '646 (U.S. 5,725,646) in view of Takayama et al. (U.S. 6,313,066).

Krishnan et al. '646 disclose lithographic ink comprising 0.5-10% rewetting agent, i.e. ethylene glycol or butyl carbitol, 2-30% pigment, amine such as monoethanolamine, 10-70% binder comprising 0-20% resin emulsion, i.e. latex obtained from (meth)acrylate and styrene, 10-70% rosin including rosin salt and maleated rosin ester, and 0-5% polyethylene imine. It is further disclosed that the ink is used in dry lithography. Attention is drawn to example 1 of Krishnan et al. '646 that discloses lithographic ink comprising 12% pigment, 5% latex, 2% monoethanolamine, 47% maleated rosin ester, and 2% polyethylene wax. It is well known as evidenced by Takayama et al. (col.9, lines 60-62) that polyethylene wax functions as plasticizer (col.1, lines 5-10, col.3, lines 15-40 and 46, col.3, line 55-col.4, line 12, and example 1). Given that Krishnan et al. '646 disclose composition identical to that presently claimed, it is clear that the composition would intrinsically be water-washable and suitable for use as wet lithographic printing ink.

While Krishnan et al. '646 fails to exemplify the presently claimed composition nor can the claimed composition be "clearly envisaged" from Krishnan et al. '646 as required to meet the standard of anticipation (cf. MPEP 2131.03), nevertheless, in light of the overlap between the

claimed composition and the composition disclosed by Krishnan et al. '646, absent a showing of criticality for the presently claimed composition, it is urged that it would have been within the bounds of routine experimentation, as well as the skill level of one of ordinary skill in the art, to use composition which is both disclosed by Krishnan et al. '646 and encompassed within the scope of the present claims and thereby arrive at the claimed invention.

14. Claim 2 is rejected under 35 U.S.C. 103(a) as being unpatentable over Krishnan et al. '646 in view of Takayama et al. as applied to claims 1 and 3-20 above, and further in view of Pennaz (U.S. 5,338,351).

The difference between Krishnan et al. '646 and the present claimed invention is the requirement in the present claims of acid number of the rosin-based resin.

Pennaz, which is drawn to inks, disclose the use of rosin possessing acid number of 25-200 and further disclose that the water-solubility or water-reducible properties of the rosin are controlled by its acid number (col.9, line 57-col.10, line 9)

In light of the above, it therefore would have been obvious to one of ordinary skill in the art to use rosin possessing acid number of 25 to 200 in Krishnan et al. '646 in order to produce rosin with desired water solubility, and thereby arrive at the claimed invention.

15. Claims 1, 5-6, 8-10, 12, and 16-20 are rejected under 35 U.S.C. 103(a) as being unpatentable over Incontro et al. (U.S. 4,973,617) in view of Navi (U.S. 4,445,433).

Incontro et al. disclose ink obtained from 50% varnish comprising 56% latex such as acrylic latex, 20% propanol, and 20% rosin-modified polyamide and 50% ink comprising 1%

amine and 36% pigment. Thus, it is calculated that the ink comprises 28% latex, 10% propanol, 0.5% amine, 18% pigment, and 10% rosin-modified polyamide. It is further disclosed that the ink contains plasticizer. Given that Incontro et al. disclose composition comprising latex, alcohol solvent, amine, pigment, rosin-based resin, and plasticizer as presently claimed, it is clear that the composition is intrinsically water-washable (col.1, lines 8-9, 40-58, and 64-66, col.2, lines 13-22 and example 2). Attention is drawn to col.4, lines 25-31 of Incontro et al. which disclose that the ink is printed using anilox roll which is well known, as evidenced by Navi (abstract), to be part of a lithographic press. Thus, it is clear that the ink of Incontro et al. is a lithographic ink and thus, intrinsically suitable as wet lithographic ink and dry lithographic ink.

While Incontro et al. fails to exemplify the presently claimed composition nor can the claimed composition be “clearly envisaged” from Incontro et al. as required to meet the standard of anticipation (cf. MPEP 2131.03), nevertheless, in light of the overlap between the claimed composition and the composition disclosed by Incontro et al., absent a showing of criticality for the presently claimed composition, it is urged that it would have been within the bounds of routine experimentation, as well as the skill level of one of ordinary skill in the art, to use composition which is both disclosed by Incontro et al. and encompassed within the scope of the present claims and thereby arrive at the claimed invention.

16. Claim 13 is rejected under 35 U.S.C. 103(a) as being unpatentable over Incontro et al. in view of Navi as applied to claims 1, 5-6, 8-10, 12, and 16-20 above, and further in view of Pugliese et al. (U.S. 3,412,053).

The difference between Incontro et al. in view of Navi and the present claimed invention is the requirement in the claims of specific type of amine.

Pugliese et al., which is drawn to the use of printing inks, disclose the use of amine such as diethanolamine or triethanolamine in order to control the drying time and stability of the ink (col.4, lines 42-59).

In light of the motivation for using specific type of amine disclosed by Pugliese et al. as described above, it therefore would have been obvious to one of ordinary skill in the art to use such amine in the ink of Incontro et al. in order to produce ink with good dry time and stability, and thereby arrive at the claimed invention.

17. The prior art made of record and not relied upon is considered pertinent to applicant's disclosure.

WO 99/27022 discloses ink comprising resin rosin, resin emulsion, amine, and pigment, however, there is no disclosure of alcohol solvent as presently claimed.

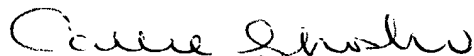
WO 01/90263 discloses water-washable ink comprising rosin, latex, pigment, and amine, however, there is no disclosure of alcohol solvent or plasticizer as presently claimed.

WO 03/042308 discloses ink comprising rosin-based resin, pigment, acid neutralizing agent, plasticizer, and latex, however, there is no disclosure of alcohol solvent as presently claimed.

18. Any inquiry concerning this communication or earlier communications from the examiner should be directed to Callie E. Shosho whose telephone number is 571-272-1123. The examiner can normally be reached on Monday-Friday (6:30-4:00) Alternate Fridays Off.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Vasu Jagannathan can be reached on 571-272-1119. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

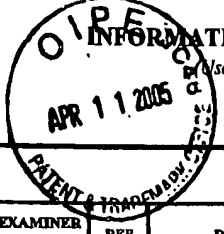
Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see <http://pair-direct.uspto.gov>. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).


Callie E. Shosho
Primary Examiner
Art Unit 1714

CS
2/3/06



Group Art Unit

 <p>INFORMATION DISCLOSURE CITATION (Use several sheets if necessary)</p>				Docket Number (Optional) C-477		Application Number 10/751,164		
				Applicant(s) Dandreaux et al.				
				Filing Date December 31, 2003		Group Art Unit 1755		
U.S. PATENT DOCUMENTS								
*EXAMINER INITIAL	REF	DOCUMENT NUMBER	DATE	NAME	CLASS	SUBCLASS	FILING DATE IF APPROPRIATE	
CS		6,444,022	09/03/02	Krishnan et al.	106	31.73		
↓		5,725,646	03/10/98	Krishnan et al.	106	31.73		
↓		3,950,290	04/13/76	Drury, Jr. et al.	260	23 EM		
U.S. PATENT APPLICATION PUBLICATIONS								
*EXAMINER INITIAL	REF	DOCUMENT NUMBER	DATE	NAME	CLASS	SUBCLASS	FILING DATE IF APPROPRIATE	
FOREIGN PATENT DOCUMENTS								
	REF	DOCUMENT NUMBER	DATE	COUNTRY	CLASS	SUBCLASS	Translation	
							YES	NO
CS		01/90263	11/29/01	WO	X	X		
CS		99/27022	06/03/99	WO				
OTHER DOCUMENTS <i>(Including Author, Title, Date, Pertinent Pages, Etc.)</i>								
EXAMINER Cacie Shusha				DATE CONSIDERED 1/31/04				

EXAMINER: Initial if citation considered, whether or not citation is in conformance with MPEP Section 609; Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

Notice of References Cited	Application/Control No. 10/751,164	Applicant(s)/Patent Under Reexamination DANDREAUX ET AL.	
	Examiner Callie E. Shosho	Art Unit 1714	Page 1 of 1

U.S. PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Name	Classification
*	A	US-6,699,312 B2	03-2004	Hayashi et al.	106/31.26
*	B	US-5,800,599 A	09-1998	Asada, Keisuke	106/31.26
*	C	US-5,338,351 A	08-1994	Pennaz, Thomas J.	524/599
*	D	US-6,313,066 B1	11-2001	Takayama, Satoshi	503/201
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(54) Title: LOW TACK WATER WASHABLE LITHOGRAPHIC PRINTING INKS

(57) Abstract: A low tack water washable lithographic printing ink composition containing water insoluble rosin resin, an oil mixture of water reducible and non-water reducible oils, pigment and a pH neutralizing agent.



LOW TACK WATER WASHABLE LITHOGRAPHIC PRINTING INKS

BACKGROUND OF THE INVENTION

5 Field of the Invention

The invention relates to low tack water washable lithographic printing ink compositions.

Description of Related Art

10 In an attempt to eliminate volatile organic compounds ("VOCs") in the pressroom, alternatives to conventional fountain based and oil based inks are being sought. Examples of useful waterbased flexographic printing inks are disclosed in U.S. Pat. No. 4,173,554 and in The Printing Ink Manual, edited by R. H. Leach and R. J. Pierce, pages 571-576, 5th edition, (Blueprint, 1993). Examples of useful
15 waterbased gravure printing inks are disclosed in U.S. Pat. Nos. 4,954,556 and 5,098,478.

The lithographic printing process has always presented unique challenges to ink formulators, since such process utilizes a planographic printing plate, wherein the image and non-image areas are in the same plane on the image carrier, and
20 two fluids are concurrently utilized to insure that ink adheres only to the image area, and not to the non-image area. In conventional lithographic printing processes, the plate is damped before it is inked with an oil based ink. Typically, the damping process utilizes a water or aqueous fountain solution, such as those described in United States Patent Nos. 3,877,372; 4,278,467; and 4,854,969. Upon damping,
25 water forms a film on the hydrophilic areas (the non-image areas) of the printing plate, but contracts into tiny droplets on the oleophilic areas (the image areas) of the plate. When an inked roller containing the oil based ink is passed over the damped plate, it is unable to ink the areas covered by the water film (the non-image areas), but will emulsify the droplets on the water repellant areas (the image areas),
30 causing such area to ink up. In the process of "offset lithography," the inked image on the plate does not directly print onto the paper substrate, but is first "offset" onto a rubber blanket, then transferred therefrom onto the paper substrate. Establishing and maintaining a correct ink/water balance during the printing process is critical,

5 and requires a high level of skill. This is one of several disadvantages associated with such printing processes, as compared to flexographic and gravure printing processes. Moreover, the oil based inks and aqueous fountain solutions typically employed in conventional offset lithographic printing processes contain fairly high levels of undesirable VOCs, generally from 30 to 45%. Further, the cleaning
10 solutions used for press wash up may also contain VOCs.

United States Patent No. 3,356,030 discloses the use of a waterbased printing ink for planographic printing utilizing a "waterless" lithographic printing plate (i.e. whose non-image areas are coated with a cured coating of a thermosetting silicone resin). However, the method entails the use of a volatile hydrocarbon
15 versus aqueous fountain solution which will coat the non-image areas and is re-applied between successive printings. Unfortunately, the use of a volatile hydrocarbon fountain solution undermines the principal purpose of using the waterbased ink compositions, namely, the avoidance or elimination of the emission of VOCs during the printing process.

20 In the 1980s, a resurgence of interest in "waterless" lithographic printing occurred. Further information about waterless printing plates and processes may be found in United States Patent Nos. 5,370,906 and 5,417,749. German Offenlegungsschrift DE 41 19 348 A1 pertains to a moistureless offset printing method which uses a waterbased printing ink. The ink described therein is one
25 which will adhere to hydrophilic materials, but not to hydrophobic materials, and contains a dye, water, 5% to 50% of a water soluble macromolecular binder, and a hygroscopic liquid, preferably a multihydric alcohol.

A method for preparing lithographic inks is described in US Patent 5,431,721 where rosins are modified with water reducible short oil alkyds, in the presence of
30 large amounts of fatty ester oils, so as to enhance water washability of an ink produced with such modified rosins. These inks are problematic in that the large amount of fatty ester oils, having molecular weights of about 300, are detrimental to the set off and drying properties of the ink immediately after printing, especially where no heat is used. In addition, the short oil alkyds used in this method are not
35 the most efficient water dispersible agents, thus resulting in inks having poor water washability unless a highly alkaline media is used (pH of 10.5-13). However, this causes corrosion problems for the press rollers and plates used in the printing process.

- 5 Other approaches have suggested the use of a humidity chamber (US Patent 5,725,646) or special rewetting agents to prevent the evaporation of water from the printing rollers (US Patent 6,444,021). The rewetting agents affect the printability of the ink, as they do not dry effectively without heat and are therefore more costly to print with. In addition these compositions require higher
- 10 concentrations of humectant or rewetting agent to achieve the desired tack stability for the ink. Further, in US Patent No. 6,444,022 the water based lithographic ink uses certain linseed oil modified resins and humectants which extinguished the need for the humidity chamber associated with waterbased inks described in US Patent 5,725,646, but the inks retained gloss and drying problems.
- 15 Accordingly there is a need for a water washable lithographic ink composition having low VOC content that uses no humectants which maintains good printability such as good tack and dynamic viscosity properties and has have high gloss, without causing any toning or set off at room temperature immediately after printing.

20

SUMMARY OF THE INVENTION

- It has now been found that the above objectives can be realized by employing a lithographic printing ink comprised of a water insoluble rosin resin dispersed in an oil mixture of non-water reducible oils and water reducible oils, a
- 25 pigment and a pH neutralizing agent.

DETAILED DESCRIPTION OF THE INVENTION

- According to the present invention it has been found that a combination of water reducible oils/polyesters and non-water reducible oils/polyesters, such as
- 30 linseed based alkyds, can be used to disperse conventional water insoluble rosin resins, having a combination of low and high acid numbers to provide ink varnishes having a stable low rating tack. When these varnishes are blended with the appropriate pigment colorants they produce water washable lithographic inks of low VOC content having excellent tack and dynamic viscosity and gloss profiles for
- 35 printing.

5 Water Insoluble Rosin Resin

The water insoluble rosin resin is made of rosin resin modified with mixtures of bifunctional non-water reducible oils/polyesters and water reducible oils/polyesters, alkyds, and the like. The water insoluble rosin resin is comprised of low and high acid number resins. The low acid number resins will have an acid number of up to about 45. The high acid number resin will have an acid number of about 45 to about 400. The water insoluble rosin resin is synthesized to be comprised of up to about 90% of low acid number resin and up to about 10% high acid number resin or to have a parts ratio of less than 1 part high acid number resin to about 9 parts low acid number resin. The water insoluble rosin resin may also include small amounts of a free flow varnish. This amount will vary depending on required flowability for the varnish or ink and is within the discretion of those skilled in the art.

Suggested water insoluble rosin resins include, but are not limited to, phenolic, maleic, fumaric, pentaerythritol, hydrocarbon resins, and/or mixtures of these groups, water insoluble resins, water soluble polyamide resins, rosin resins, rosin salts, tall oil resins, methacrylic resins, styrene-acrylic resins, polystyrenesulfonic acid and its salts, and acrylic or vinyl emulsion polymers prepared from monomers selected from the group consisting of acrylic acid esters, fatty acid esters, methacrylic acid esters, acrylic acid esters of polyhydric alcohols, methyl methacrylate, styrene, vinyl styrene, and vinyl acetate, and mixtures thereof. The rosin resins may be gelled and/or free flowing resins. Preferred rosin resins are Filtrez 615, Filtrez 681, Albertol KP410, Albertol KP700, Albertol KP767, all manufactured by Akzo-Nobel Chemicals, Inc., Chicago, IL. The above mentioned rosin resins are representative of high molecular weight modified rosin resins have low compatibility in mineral oils and are soluble in 2-ethylhexyltallate, fatty ester acid based oils. A variety of other conventional rosin resins can be used and are readily known to those of ordinary skill in the art.

Oil Mixture

It has been discovered that a variety of environmentally acceptable non-water reducible oils such as fatty acid ester oils and in particular 2-ethylhexyltallate, fatty ester acid based oils and Magiesol oils, such as Magie Sol 62 (manufactured by Magie Brothers Oil, Franklin Park, IL.) and the like, can be used in small amounts (less than 10 wt.%) to adjust the flowability and viscosity of a water washable lithographic printing ink composition. These non-water reducible oils have low

- 5 molecular weight (less than 300), and are readily adsorbed by the substrate to provide quick setting and drying inks. The use of non-water reducible oils and/or polyesters in their unreacted form solubilize the water insoluble rosin resin. If the viscosity of the resulting ink varnish is high the amount of oil can be used to adjust and help in manufacturability and printability.
- 10 The water washable lithographic printing ink composition of the present invention contains a mixture of oils comprised of both water reducible and non-water reducible oils. The water reducible oil and/or polyester mixtures comprise the reaction product of various glycols or polyglycols and linseed or other vegetable oil. They may also include lithium ricinoleate, phthalic anhydride and triphenyl
- 15 phosphate. Other water reducible oils for use in the present invention, include, but are not limited to, modified or unmodified oils, linseed oil, olive oil, castor oil, soybean oil, other vegetable oils, and mixtures thereof. Preferred water reducible oils polyesters are modified linseed oils such as DV 1469 DVPED200, both manufactured by Reichold Inc., Durham, NC., alcohol modified linseed oils such as
- 20 Resydrol Val 5227W, manufactured by Akzo-Nobel Chemicals, Inc., Chicago, Il., maleinized linseed oils such as Maleinized ARLO, manufactured by Degan Oil, Jersey City, NJ, and modified linseed oils with methoxy alcohol such as Maleated ARLO, manufactured by Sun Chemical, Ft. Lee, NJ. The water reducible oils/polyesters may be added to the composition directly or contained in the
- 25 pigment flush (up to 50% of the pigment flush may contain water reducible oils/polyesters). The non-water reducible oils polyester mixtures of the present invention include, but are not limited to, fatty acid ester oil groups and MagieSol oils, such as Magie Sol 62 (manufactured by Magie Brothers), modified soy oils, phthallate ester oils, tallate esters, petroleum oils, and mixtures thereof. Preferred
- 30 non-water reducible oils include petroleum based oils such as Magie Oil 500 and MagieSol 62, both manufactured by Magie Brothers Oil, Franklin Park, Il.; fatty acid ester oils such Nirez 9012, manufactured by Arizona Chemicals, Jacksonville, Fl.; phthalate ester oils such as Estisol 256 and Estisol 312, both manufactured by Haltermann GmbH, Hamburg, Germany; tallate ester oils such as 2EH Tallate,
- 35 manufactured by Chemol, Inc., Greensboro, NC; and modified soy oils such as Vikoflex, manufactured by Elf-Atochem, King of Prussia, Pa. One of ordinary skill in the art will routinely know how to vary the quantity and ratio of water reducible and non-water reducible oils/polyesters of the lithographic ink composition in order to achieve the desired tack and dynamic viscosity for a specific ink composition.

5 Pigment

Pigments which may be incorporated into the rosin resin ink vehicle include all of those conventionally used and any dye, pigment, filler, or the like, which can be bonded to the rosin resin and permit the resultant resinated pigment to be dispersed, milled, mixed, blended, or dissolved in any conventional manner in forming the ink composition. In addition to the pigment, the composition may also contain a blend of conventional resins used as binder resins for pigments. Conventional pigment binder resins may include those sold under the GAX™ mark by FiltzChemicals Corporation, Elmhurst, Illinois, U.S.A. . Examples of such pigments include the Color Index Pigments (C.I. Pigments) listed in the table below:

Pigment Generic Name	Pigment C.A. Index/Chemical Name
C.I. Pigment Yellow 17	Butanamide, 2,2'-[(3,3'-dichloro[1,1'-biphenyl] 4,4'-diyl)bis(azo)bis [N-(2-methoxyphenyl)-3-oxo-
C.I. Pigment Blue 27	Ferrate (4-1), hexakis (cyano-C)-ammonium iron (3+)(1:1:1)
C.I. Pigment Red 49:2	1-Naphthalenesulfonic acid, 2-[(2-hydroxy-1-naphthalenyl)azo]-, calcium salt (2:1)
C.I. Pigment Red 81:	Benzoic acid, 2-[6-ethyl-amino)-3-(ethylimino)-2,7-dimethyl-3H-xanthen-9-yl]-, ethyl ester, w/molybdenum tungsten hydroxide oxide phosphate
C.I. Pigment Red 81:3	Benzoic acid, 2-[6-ethyl-amino)-3-(ethylimino)-2,7-dimethyl-3H-xanthen-9-yl]-, ethyl ester, molybdatesilicate
C.I. Pigment Red 81:x	Benzoic acid, 2-[6-(ethyl-amino)-3-(ethylimino)-2,7-dimethyl-3H-xanthen-9-yl]-, ethyl ester, molybdatephosphate
C.I. Pigment Yellow 83	Butanamide, 2,2'-[(3,3'-dichloro[1,1'-biphenyl]-4,4'-diyl)bis(azo)bis[N-(4-chloro-2,5-dimethoxy-phenyl)-3-oxo-
C.I. Pigment Violet 23	Diindolo[3,3',2'm] triphenodioxazine, 8,18-dichloro-5,15-diethyl- 5,15-dihydro-
C.I. Pigment Red 49:1	1-Naphthalenesulfonic naphthalenyl)azo]-, barium salt (2:1)
C.I. Pigment Red 57:1	2-Naphthalenecarboxylic acid, 3-hydroxy-4-[(4-methyl-2-sulphophenyl)azo]-, calcium salt (1:1)
C.I. Pigment Blue 61	Benzenesulfonic acid, [[4-[(4-phenylamino)-phenyl]-[4-(phenylimino)-2,5-cyclohexadien-1-ylidene]methyl]-phenyl] amino]-
C.I. Pigment Red 48:1	2-Naphthalenecarboxylic acid, 4-[(5-chloro-4-methyl-2-sulphophenyl)azo]-3-hydroxy-, barium salt (1:1)
C.I. Pigment Red 52:1	2-Naphthalenecarboxylic acid, 4-[(4-chloro-5-methyl-2-sulphophenyl)azo]-3-hydroxy-, calcium salt (1:1)
C.I. Pigment Violet 1	Ethanaminium, N-[9-(2-Carboxyphenyl)-6-(diethyl-amino)-3H-xanthen-3-ylidene]-N-ethyl-, molyb-Datetungstatephosphate
C.I. Pigment White 6	Titanium oxide (TiO ₂)

C.I. Pigment Blue 15	Copper, [29H, 31H-phthalocyaninato (2-)-N ²⁹ , N ³⁰ , N ³¹ , N ³²]-, (Sp-4-1)
C.I. Pigment Yellow 12	Butanamide, 2,2'-[(3,3'-dichloro[1,1'-biphenyl]-4,4'-diyl)bis(azo)]bis[3-oxo-N-phenyl]-
C.I. Pigment Blue 56	Benzenesulfonic acid, 2-methyl-4-[[4-[(3-methylphenyl)amino] phenyl]-[4-[(3-methyl-phenyl)-Imino]-2-5-cyclohexadien-1-ylidene)methyl]-phenyl] amino]-
C.I. Pigment Orange 5	2-Naphthalenol, 1-[(2,4-dinitrophenyl)azo]-
C.I. Pigment Black 7	Carbon black
C.I. Pigment Yellow 14	Butanamide, 2,2'-[(3,3'-dichloro[1,1'-biphenyl]-4,4'-diyl)bis(azo)]bis-[N-(2-methylphenyl)-3-oxo-
C.I. Pigment Red 48:2	2-Naphthalenecarboxylic acid, 4-[(5-chloro-4-methyl-2-sulfo-phenyl)-azo]-3-hydroxy-, calcium salt (1:1)
C.I. Pigment Blue 15:3	Copper, [29H, 31H-Phthalocyaninato (2-)-N ²⁹ , N ³⁰ , N ³¹ , N ³²]-, (SP-4-1)-
C.I. Pigment Yellow 1	Butanamide, 2-[(4-methyl-2-nitrophenyl)azo]-3-oxo-N-phenyl-
C.I. Pigment Yellow 3	Butanamide, 2-[(4-chloro-2-nitrophenyl)azo]-N-(2-chlorophenyl)-3-oxo-
C.I. Pigment Yellow 13	Butanamide, 2,2'-[(3,3'-dichloro[1,1'-biphenyl]-4,4'-diyl)bis(azo)]bis [N-(2,4-dimethylphenyl)-B- oxo-
C.I. Pigment Orange 16	Butanamide, 2,2'-[(3,3'-dimethoxy[1,1'-biphenyl]-4,4'-diyl)bis(azo)]bis [3-oxo-N-phenyl-
C.I. Pigment Yellow 55	Butanamide, 2,2'-[(3,3'- dichloro[1,1'-biphenyl]-4,4'-diyl)bis(azo)]bis [N-(4-methylphenyl)-3-oxo-
C.I. Pigment Red 41	3H-Pyrazol-3-one, 4,4'-[(3,3'-dimethoxy[1,1'-biphenyl]-4,4'-diyl)bis (azo)]bis[2,4-dihydro-5-methyl-2-phenyl-
C.I. Pigment Orange 34	3H-Pyrazol-3-one, 4,4'-[(3,3'-dichloro[1,1'-biphenyl]-4,4'-diyl)bis (azo)]bis[2,4-dihydro-5-methyl-2-(4-methylphenyl)]
C.I. Pigment Blue 62	4,4'-Bis(diethylamino) benzophenone condensed with N-ethyl-1-naphthyl-amine in toluene with phosphorous oxychloride and converted to the copper ferrocyanide salt (PTMA salt in P.Blue 1)
C.I. Pigment Red 22	2-Naphthalenecarboxamide, 3-hydroxy-4-[(2-methyl-5-nitrophenyl)azo]-N-phenyl-
C.I. Pigment Red 170	2-Naphthalenecarboxamide, 4-[[4-(aminocarbonyl) phenyl]azo]-N-(2-ethoxy-phenyl)-3-hydroxy-
C.I. Pigment Red 88	Benzo[b]thiophen-3(2H)-one, 4,7-dichloro-2-(4,7-dichloro-3-oxobenzo[b]thien-2(3H)-ylidene)-
C.I. Pigment Yellow 151	A diazotized aniline derivative coupled with an acetoacetyl derivative of 5-aminobenzimidazolone
C.I. Pigment Red 184	A diazotized substituted aniline coupled with a derivative of 3-hydroxy- 2-naphthanilide
C.I. Pigment Blue 1:2	Ethanaminium, N-[4-[[4-(diethylamino)phenyl] [4-(ethylamino)-1-1 naphthalenyl]methylene]-2,5-cyclohexadien-1-ylidene]-N-ethyl-, [orthosilicato(4-)] hexatriacontaoxo-dodecamolybdate(4)-(4:1)

5

C.I. Pigment Blue 15:1	Copper,[29H,32H-phthalocyaninato(2-)-N ²⁹ , N ³⁰ , N ³¹ , N ³²]-, (SP-4-1)- or Copper,[chloro-29H, 31H-phthalocyaninato (2-1)-N ²⁹ , N ³⁰ , N ³¹ , N ³²]-
C.I. Pigment Red 23	2-Naphthalenecarboxamide, 3-hydroxy-4-[(2-methoxy-5-nitrophenyl)azo]-N-(3-nitrophenyl)
C.I. Pigment Red 3	2-Naphthalenol, 1-[(4-methyl-2-nitrophenyl)azo]-
C.I. Pigment Yellow 126	A tetrazotized derivative of 3,3-dichlorobenzidine coupled with a derivative of acetoacetanilide
C.I. Pigment Red 169	3-Ethylamino-p-cresol condensed with phthalic anhydride, esterified with ethanol and a mineral acid, and converted to the copper ferrocyanide complex (chloride salt is C.I. Basic Red 1, PTMA salt is P.Red 81:1)
C.I. Pigment Orange 13	3H-Pyrazol-3-one, 4,4'-[(3,3'-dichloro [1,1'-biphenyl]-4,4'-diyl)bis(azo)]bis[2,4-dihydro-5-methyl-2-phenyl]
C.I. Pigment Red 10	2-Naphthalenecarboxamide, 4-[(2,5-dichlorophenyl) azo]-3-hydroxy-N-(4-methylphenyl)
C.I. Pigment Blue 1:X	Ethanaminium, N-[4-[[4-(diethylamino)phenyl] [4-(ethylamino)-1-naphthalenyl]methylene]-2,5-cyclohexadien-1-ylidene]-N-ethyl-, molybdate-phosphate
C.I. Pigment Yellow 42	Iron oxide (Fe ₂ O ₃) hydrate
C.I. Pigment Red 101	Iron oxide (Fe ₂ O ₃)
C.I. Pigment Brown 6	Iron oxide (Fe ₂ O ₃), some FeO and Fe ₂ O ₃ ·H ₂ O
C.I. Pigment Brown 7	Iron oxide (Fe ₂ O ₃) plus varying amounts of clay
C.I. Pigment Brown 7:X	Fe ₂ O ₃ x MnO ₂ with varying amounts of clay
C.I. Pigment Metal 1	Aluminum
C.I. Pigment Black 11	FeO·Fe ₂ O ₃
C.I. Pigment Metal 2	Copper, zinc
C.I. Pigment Red 112	2-Naphthalenecarboxamide, 3-hydroxy-N-(2-methyl-phenyl)-4-[(2,4,5-tri-chlorophenyl)azo]-

The pigment may be added to the lithographic printing ink composition in either dry powder, flush, presscake, or water based dispersion form.

10 pH Neutralizing Agent

The composition of the present invention also contains a neutralization agent to neutralize the pH of the water insoluble resin, be it either acidic or basic in

5 nature. The pH neutralizing agent may also solubilize the high acid number water insoluble rosin resin. Acid pH neutralizing agents are selected from primary amines, secondary amines and/or tertiary amines such as: monoethanolamine, diethanolamine, triethanolamine, N-dimethylethylamine, dimethylethanolamine, methyldiethanolamine, polyethylene imine, triethylanolamine, propylene diamine,
10 hexamethylene amine, hexamethylene diamine, urea, dibutyl amine, diethylene triamine, and mixtures thereof. Preferred acid pH neutralizing agents include monoethanolamine and hydroquinone. The above pH neutralizing agents are representative candidates of a variety of pH neutralizing agents both basic and acidic which can be used by those of ordinary skill in the art.

15

Additives

The water washable lithographic printing inks of the present invention may also incorporate water to act as a rheology and/or a surface energy modifier of the ink composition and to enhance the water washability of the ink. The water may be
20 an added component or be contributed by one of the other components of the composition such as residual water from a pigment flush or presscake.

The water washable lithographic printing ink may also include a nonionic surfactant selected from any used routinely in the art for ink and ink-related applications. The nonionic surfactants may be present in the ink composition of the
25 invention in an amount such that the dynamic surface tension of the total composition is about 20 to about 40 dynes/cm. Examples of suitable nonionic surfactants include acetylenic glycols, ethoxylated glycols, sorbitan esters, and mixtures thereof. Particularly preferred are ethoxylated acetylenic diols. Preferred surfactants include, for example, SURFYNOL®, manufactured by Air Products and
30 Chemicals, Inc., Allentown, Pennsylvania, U.S.A., and DISPERBYK®, manufactured by BYK Chemie, Wesel, Germany.

The ink may also contain a clay such as natural clay, or synthetic clay, such as synthetic layered silicate or hectorite, or mixtures thereof. Suitable synthetic clays include those in either gel-forming grades or sol-forming grades, although gel-
35 forming grades are preferred. Suitable synthetic clays for use in the present invention, include laponites (a synthetic layered silicate) available, for example, from Laporte Industries, Ltd., United Kingdom. The clay when present in the invention, is used in an amount sufficient to achieve desired rheological properties of the ink composition.

5 The ink composition may also contain additional additives such as but are not limited to, waxes, for example, Jon Wax 26, Jon Wax 120 (available from S.C. Johnson & Sons, Inc., Racine, Wisconsin, U.S.A.), or Van Wax 35 (available from Vantage, Garfield, New Jersey, U.S.A.); modifiers for example, defoamers such as Resydrol (available from Vantage); Carbowet 990 (available from Vantage); Aerosol
10 (available from McIntyre, Chicago, Illinois, U.S.A.). Finally, the ink composition may include alcohols such as N-propyl alcohol, isopropyl alcohol, propylene glycol, ethylene glycol monobutyl ether, or ethylene glycol; biocides; pH stabilizers; fatty acid esters; gellants; driers; dispersants; and thickeners such as acrysol RM-825 (available from Rohm and Haas, Philadelphia, Pennsylvania, U.S.A.).

15

The Printing Ink Composition

 The water washable lithographic printing ink composition of the present invention contains 30% to about 50% by weight of water insoluble rosin resin dispersed in a mixture of non-water reducible oils and/or polyesters and water
20 reducible oils and/or polyesters. The combination is cooked at 160-260°C (wet or dry) for approximately 15-30 minutes. The rosin resin as previously mentioned can vary in acid number from 0-200 or higher. The mixture of non-water-reducible and/or reducible oils has "high solvency" power for the rosin resin. The ink composition also contains a pH neutralizing agent, a pigment and optionally up to
25 about 25 wt.% water. Further additions may include a non-ionic surfactant in an amount sufficient to lower the dynamic surface tension of the total composition from about 20 to about 40 dynes/cm, and wax. One of ordinary skill in the art will routinely know to vary the quantities of each of the above component of the printing ink composition to achieve the desired printable properties.

30 The printing ink composition may contain water insoluble rosin resin in an amount up to about 90 wt.%. It is preferable that the rosin resin be present in an amount of up to about 60 wt.% and most preferred that the rosin resin be present in an amount of about 12 wt.% to about 35 wt.%. One of ordinary skill in the art will know to vary the amount of rosin resin in the ink composition in order to achieve
35 the desired tack and rheology for a specific ink composition.

 The oil mixture can contain up to about 70% of water reducible oil and up to about 90% of non-water reducible oil. The oil mixture may contain a ratio of at least 1 part of water reducible oil to 9 parts of non-water reducible oil. It is preferred that the oil mixture be present in an amount of up to about 70 wt.%, more preferred that

- 5 the oil be present in an amount of up to about 45 wt.%, and most preferred that the oil be present in an amount of about 15 wt.% to about 45 wt.%.

In general, it is preferred that the ratio of water insoluble rosin resin to pigment is in the range of about 1 parts pigment to about 8 parts water insoluble rosin resin to about 1 parts pigment to about 1 parts water insoluble rosin resin
10 (about 1:8 to about 1:1 parts). It is more preferred that the ratio of pigment to water insoluble rosin resin is about 1 parts pigment to about 4 parts water insoluble rosin resin (about 1:4 parts). Overall, the pigment may comprise up to about 50 wt.% of the overall composition.

It is preferred that the pigment be present in the ink composition in the
15 amount of up to about 40 wt.% and more preferred that the pigment be present in an amount of up to about 30 wt.%. A person of ordinary skill in the art will recognize that the amount of pigment present in the ink composition of the present invention will vary, depending on several factors, including the desired opacity of the end product.

20 It is preferred that the pH neutralizing agent be present in the ink composition in the amount of up to about 10 wt.% and more preferred that the pH neutralizing agent be present in an amount of up to about 8 wt.%. One of ordinary skill in the art will know to vary the quantity of the pH neutralizing agent based on the desired viscosity and rheology of the ink.

25 While water can be incorporated in the printing ink composition in an amount up to about 25 wt.%, a preferred amount is up to about 10 wt.% and a more preferred amount is up to about 5 wt.%.

It is contemplated that the selected nonionic surfactant(s) may be present in the ink composition in an amount of about 0.1 wt.% to about 5 wt.%. It is preferred
30 that the nonionic surfactant(s) be present in the ink composition in an amount of about 0.1 wt.% to about 2 wt.%.

It is preferred that the selected clay be present in an amount of up to about 10 wt.%, or up to about 5 wt.%.

The final ink composition is washable with water (pH=8) or slightly alkaline
35 detergents such as ZEP, manufactured by ZEP Corporation, or water containing dispersible surfactants. Furthermore, high gloss (40-70) is obtainable due to the appropriate rheology in these ink compositions. Different levels of VOCs are possible depending on the composition. Thus, inks with less than 15 wt.% or 10

- 5 wt.%, or 5 wt.%, or even less than 1 wt.% of VOC content can be made and still maintain reasonable tacks.

The physical characteristics of the ink composition include tack between 11-23 (1200 rpm and 90°F), tan (viscous versus elastic flow to establish gloss development) of about 2 and viscosities in the range of 48 Pas (at 100s⁻¹).
10 However, higher or lower viscosities are possible. In addition, continuous flow experiments in a controlled stress rheometer showed that ink compositions with good gloss had a yield stress of 0-100 Pa according to the H-B model applied in the 0.1-100 s⁻¹ shear rate region. However, the range of values of the rheological parameters is not limited to the values reported herein.

15 The water washable ink composition of the present invention dries rapidly and at a rate comparable to that achieved by conventional fountain solution oil based solvent ink systems and has low tack, emits reduced levels of volatile organic compounds (VOCs), and has a high gloss. The ink composition has no set off at room temperature after 0-5 minutes, which is also equal to that for inks using
20 solvents and having a high VOC content. Thus, the present inks are as quick drying as conventional solvent based inks while being environmentally safer to produce. They also have a softer body versus that of the solvent based ink, and therefore can be handled more easy during manufacturing and have excellent printability while maintaining excellent gloss, without edge picking/pulling, and offer
25 good fade resistance and press stability when compared to conventional solvent based inks. In addition, the inks of the present invention can be transferred with conventional multiple roller systems and remain open when subjected to dynamic stress, resulting in an improved roller stability in comparison with the inks of the prior art. The setting times of the printed final product using the ink composition can
30 vary from up to 5 minutes to up to 15-20 minutes. It has been found that, in general, the high gloss of the final printed ink composition on a substrate can be maintained at fast-setting rates and good set off can be achieved in the same time frame.

The water washable ink compositions of the present invention are further illustrated by the following non-limiting examples in which all parts and percentages
35 of components are by weight and based on the total weight of the composition, unless otherwise indicated.

5

Example 1 (Comparative)

Comparative water washable lithographic inks (containing only water reducible oils and not a mixture of oils) were prepared from the components indicated below:

10

Table I

Component	Composition						
	A	B	C	D	E	F	G
Cyan Flush containing up to 50% water reducible oil	58.8	57.3	58.8	----	----	----	58.8
Magenta Flush containing up to 50% water reducible oil	-----	-----	-----	57.8	56.8	57.8	----
Rosin resin in water reducible oil	39 ^(a)	37.5 ^(b)	31 ^{(a) & (b)} in 50:50	31 ^(a)	30 ^(a)	31 ^(a)	31 ^(a)
Non-water reducible oil	-----	-----	5 ^(c)	6 ^(d)	8 ^(d)	----	----
Neutralizing agent (acid)	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Fatty acid ester	-----	-----	-----	-----	-----	6 ^(e)	5 ^(e)
Driers	2	2	2	2	2	2	2
Gellant	-----	3	3	3	3	3	3
Total	100	100	100	100	100	100	100

^(a) Filtrez 615 (30 wt.%), manufactured by Akzo-Nobel Chemicals, Inc., Chicago, IL, a phenolic modified rosin, in DV 1469 (70 wt.%), manufactured by Reichold Inc, Durham, NC; a modified linseed oil.

15

^(b) Filtrez 681 (30 wt.%), manufactured by Akzo-Nobel Chemicals, Inc., Chicago, IL, a phenolic modified rosin ester, in DV 1469 (70 wt.%), manufactured by Reichold Inc, Durham, NC; a modified linseed oil.

20

^(c) Magie Oil 500, manufactured by Magie Brothers Oil, Franklin Park, IL, a petroleum based oil.

^(d) MagieSol 62, manufactured by Magie Brothers Oil, Franklin Park, IL, a petroleum based oil.

^(e) Nirez 9012, manufactured by Arizona Chemicals, Jacksonville, FL, a fatty acid ester oil.

Example 2 (Comparative)

25

Prints were made on a Didde press using the lithographic inks of Example 1 and a web substrate of 60# coated paper. The magenta colored ink compositions (A, B, C and G) and the cyan colored compositions (D, E, and F) resulted in printed sheets that dried instantly at an elevated web temperature of 300°F. The resulting gloss of the magenta colored printed sheets was 42-50.

30

Example 3 (Comparative)

The comparative inks in Example 1 were printed on a coated substrate using a Miehle press. The tack for the ink was measured using a Tackmaster 92 (manufactured by Kershaw Instrumentation, Swedsboro, NJ) operating at a speed of 1200 rpm at 70°F. These test results are set forth below:

35

5

Table II

Component	Composition						
Properties	A	B	C	D	E	F	G
Tack (1-5 min.)	22.6-23.4	22.4	23-23.8	22.8-23.1	21-21.7	21.3-22.7	23.3-23.3
Viscosity (Pas@100s ⁻¹)	34	34	48	48	48	44	56
VOC content	0	0	4	2	3	0	0

The printed substrates dried in 15-20 minutes at room temperature and had a resulting gloss of up to 45-50. The magenta colored printed sheets (D, E, and F) were tack free within 3-4 minutes at a web temperature of 270°F and had minimal tack at a web temperature of 150°F within 15-20 minutes. However, the viscosity of the magenta colored print sheets was high. In contrast, the cyan colored printed sheets (A, B, C and G) had lower viscosity but a higher tack, which disrupts effective printing. The inks were washable with ZEP cleaning solution, manufactured by ZEP Corporation.

The Miehle press trial established the feasibility of making a fast drying water washable system that is very low in VOCs (<5%). However, a faster drying ink with low tack was still needed and continued experimentation using a mixture of water reducible and non-water reducible oils was undertaken.

Example 4

Water washable lithographic inks were prepared from the components indicated below:

Table III

Component	Composition						
	A	B	C	D	E	F	G
Magenta Flush containing up to 50% water reducible oil	50	50	53	55	52	55	55
Rosin resin and non-water reducible oil	45 ^(a)	45 ^(a)	42 ^(b)	38 ^(c)	31 ^(d)	38 ^(e)	38 ^(c)
pH neutralizing agent ^(f)	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Driers	2	2	2	2	2	2	2
Gellant	2.8	2.8	2.8	2.8	2.8	2.8	2.8
Wax	----	----	----	2	2	2	2
Total	100	100	100	100	100	100	100

30

^(a) Albertol KP410 (32.3 wt.%), manufactured by Akzo-Nobel Chemicals, Inc., Chicago, IL, a Resol modified rosin resin, in Estisol 256 (67.7 wt.%), manufactured by Haltermann GmbH, Hamburg, Germany, a 2-ethylhexanoate coconut oil.

- 5 ^(b) Albertol KP410 (wt.%), manufactured by Akzo-Nobel Chemicals, Inc., Chicago, Il., a Resol modified rosin resin, in Estisol 256 (wt.%), manufactured by Haltermann GmbH, Hamburg, Germany, a 2-ethylhexanoate coconut oil, in DV 1469 (wt.%), manufactured by Reichold Inc, Durham, NC, a modified linseed oil.
- 10 ^(c) Albertol KP410 (wt.%), manufactured by Akzo-Nobel Chemicals, Inc., Chicago, Il., a Resol modified rosin resin, in Estisol 256 (wt.%), manufactured by Haltermann GmbH, Hamburg, Germany, a 2-ethylhexanoate coconut oil, in Vikoflex (wt.%), manufactured by Elf-Atochem, King of Prussia, PA, a modified soy oil.
- 15 ^(d) Filtrez 681 (wt.%), manufactured by Akzo-Nobel Chemicals, Inc., Chicago, Il., a phenolic modified rosin ester, in Estisol 256 (wt.%), manufactured by Haltermann GmbH, Hamburg, Germany, a 2-ethylhexanoate coconut oil, in DVPED200 (wt.%), manufactured by Reichold Inc, Durham, NC, a modified linseed oil.
- 20 ^(e) Albertol KP410 (wt.%), manufactured by Akzo-Nobel Chemicals, Inc., Chicago, Il., a phenolic modified rosin ester, in Estisol 312 (wt.%), manufactured by Haltermann GmbH, Hamburg, Germany, a 2-ethylhexyl ester oil, in DV 1469 (wt.%), manufactured by Reichold Inc, Durham, NC, a modified linseed oil.
- ^(f) Monoethanolamine, manufactured by Dow Chemical, Midland, Mi., an amine.
-

Example 5

- 25 The ink compositions of Example 4, containing mixtures of water reducible and non-water reducible oils, were printed on a substrate using a Miehle press. The tack was measured using a Tackmaster 92 as described in Example 3. These results are set forth below:

Table IV

Component	Composition						
Properties	A	B	C	D	E	F	G
Tack (1-5 min.)	11.6-14.1	16.7-19.1	15.4-17.2	19.3-20.9	20.1-20.9	20.1-21.1	16.6-16.6
Viscosity (Pas@100s ⁻¹)	-----	>35	-----	33	>>33	-----	-----
VOC content	30%	27%	<15%	10%	9%	<4%	<4%
Gloss/Prufbau	-----	-----	44	44	46	41	48

30

- The volatile organic compound ("VOC") content of the ink was generally less than 15 wt.% and no toning occurred on the Miehle Press. The inks immediately set on the printed substrate at 270°F Sinvatrol oven temperature (65°C web temperature). Example 4 produced inks having substantially less overall tack than
- 35 that of the water reducible oil only inks of Comparative Examples 1-3. In addition, the inks of Example 4 exhibited superior setting properties than those in Comparative Examples 1-3 improved gloss.

Example 6

- 40 Water washable magenta colored printing ink compositions were developed using varied rosin resins and oil mixtures, as set forth below.

5

Table V

Component	Composition								
	A	B	C	D	E	F	G	H	I
Magenta Flush containing up to 50% water reducible oil	41	41	41	41	41	41	40	40	42.5
Rosin resin and non-water reducible oil	46.5 ^(a)	46.5 ^(a)	46.5 ^(a)	46.5 ^(a)	46.5 ^(a)	46.5 ^(b)	45 ^(b)	45 ^(b)	55 ^(b)
Water reducible oil	10 ^(c)	10 ^(d)	10 ^(e)	10 ^(f)	10 ^(g)	10 ^(d)	12.5 ^(c)	10.5 ^(c)	0
pH neutralizing agent ^(h)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Surfactant	-----	-----	-----	-----	-----	-----	-----	2.0	-----
Drier	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Total	100	100	100	100	100	100	100	100	100

10 ^(a) Albertol KP700 (45 wt.%), manufactured by Akzo-Nobel Chemicals, Inc., Chicago, IL, a high molecular weight modified rosin resin (low compatibility in mineral oils), in 2-ethylhexyltallate (55 wt.%), a fatty ester acid based oil.

^(b) Albertol KP767 (45 wt.%), manufactured by Akzo-Nobel Chemicals, Inc., Chicago, IL, a very high molecular weight modified rosin resin (extremely low compatibility in mineral oils), in 2-ethylhexyltallate (55 wt.%), a fatty ester acid based oil.

15 ^(c) Resydrol Val 5227W, manufactured by Akzo-Nobel Chemicals, Inc., Chicago, IL, an alcohol modified linseed oil.

^(d) Maleinized Tung Oil, manufactured by Degen Oil, Jersey City, NJ.

^(e) DV1469, manufactured by Reichold Inc, Durham, NC, a modified linseed oil.

^(f) Maleinized ARLO, manufactured by Degen Oil, Jersey City, NJ, a maleinized linseed oil.

20 ^(g) Maleated ARLO, made by Sun Chemical, Carlstadt, NJ, a modified linseed oil with methoxy alcohol.

^(h) Hydroquinone, manufactured by Akzo-Nobel Chemicals, Inc., Chicago, IL, an amine.

Example 7

25 Then inks of Example 6 above were printed using a Miehle press on a coated substrate. The tack was measured as described in Example 3. Print density was measured using an ExRite Densitometer (manufactured by ExRite of Granville, Mi.). These results are set forth below:

30

Component Properties	Composition								
	A	B	C	D	E	F	G	H	I
Tack at 1 min.	14.6	14.7	14.5	14.4	14.3	14.7	13.8	13.7	14.2
Tack at 5 min.	14.7	14.9	14.6	13.5	14.4	14.6	13.9	13.9	14.2
Viscosity (poise/2500s ⁻¹)	225.6	243.6	272.9	-----	282.2	526.9	379.2	378.5	258.4
Print density	1.47	1.46	1.50	1.47	1.52	1.45	1.44	1.44	1.48
Gloss	36.5	42.1	39.4	31.7	44.1	34.7	32.2	31.7	36.9
Set Off	Good	Good	Good	Good	Good	Good	Poor	Good	Good

It was observed that the tack of Example 6 inks was substantially reduced as compared to conventional solvent based inks and the viscosity was superior. In

5 addition, the setting, drying and gloss properties of Example 6 Inks were comparable to that offered by conventional solvent inks (having high VOC content). Specifically, the inks of Example 6 provided no set-off using both coated and uncoated substrates within the same time frame as solvent based inks. Further, the inks dried within the same time frame as expected for conventional solvent
 10 based inks, and $\tan(\delta)$ of 1-2 were obtained consistent with gloss development. The inks also had a gloss measurement higher than that of conventional solvent based inks and printed without toning or the observance of edge picking. The inks were washed from the press as described in Example 3 and the observed water washability for the inks was excellent.

15 Overall, the underlying varnishes (rosin resins and oil mixtures without the pigment) used to formulate the inks of Example 6 provided very low and extremely low compatibility in fatty mono-esters, while maintaining high viscosities and molecular weights. The ink tack was as low as 8-10. In general, the inks provided higher viscosity than conventional solvent based inks.

20 Of the oil mixtures used, the modified linseed oil with alcohol (Example 7C) exhibited superior performance to the maleinized tung oil (Examples 7B, 7G, 7H, and 7I). The modified linseed oil (Examples 7D and 7E) provided the best results in low tack without reducing the gloss and water washability for the ink. The maleinized linseed with alcohol (Example 7A) exhibited the best water washability.

25

Example 8

A water washable lithographic ink was prepared from the components indicated below:

30

Component	
Rosin resin ^(a)	24
Water reducible oil ^(b)	26
Non-water reducible oil ^(c)	17.5
Dry Pigment (Carbon Black)	15
Acid neutralizing agent ^(d)	0.6
Fatty ester acid	2
Alkyd	6
Gellant	1.5
Wax	4
Driers	2
Anti-oxidant	0.5
TOTAL	100

- 5 ^(a) Albertol KP700 (45 wt.%), manufactured by Akzo-Nobel Chemicals, Inc., Chicago, IL, a high molecular weight modified rosin resin (low compatibility in mineral oils), in 2-ethylhexyltallate (55 wt.%), a fatty ester acid based oil.
- ^(b) DV1469, manufactured by Reichold Inc, Durham, NC, a modified linseed oil; Resydrol Val 5227W, manufactured by Akzo-Nobel Chemicals, Inc., Chicago, IL, an alcohol modified linseed oil.
- 10 ^(c) 2 EH Tallate, manufactured by Chemol Inc., Greensboro, NC, a 2-ethyl-hexyl-tallate for non-water reducible oil.
- ^(d) MEA, manufactured by Dow Chemical, Midland, Mi., a monoethanolamine amine
-

15 The ink of Example 8 was run on various printing presses which include a Komori 40, a Heidelberg SM 74, a Mitsubishi and a OMCSA press. Typical printing runs produced 1,000-160,000 prints. No toning at the start or pulling was observed, which resulted in less paper waste. The prints provided no set off when both coated and uncoated substrates were used, which is comparable to that of

20 conventional solvent based inks. The gloss level of the inks was the same as that provided by conventional solvent based inks. The inks allow the use of air dried water based coatings since they are low in VOC content. Finally, the inks were washed from the press as described in Example 3 and the observed water washability was excellent.

25 It will be appreciated by those skilled in the art that changes could be made to the embodiments described above without departing from the broad inventive concept thereof. It is understood, therefore, that this invention is not limited to the particular embodiments disclosed, but it is intended to cover modifications within the spirit and scope of the present invention as defined by the appended claims.

30

5

CLAIMS

We claim:

1. A water washable lithographic printing ink composition comprising:
 - (a) water insoluble rosin resin;
 - (b) an oil mixture of water reducible and non water-reducible oils;
 - (c) pigment; and
 - (d) a pH neutralizing agent.
2. The composition of claim 1 wherein the amount of water insoluble rosin resin present is up to about 90 wt.%.
3. The composition of claim 1 wherein the amount of water insoluble rosin resin present is up to about 60 wt.%.
4. The composition of claim 1 wherein the amount of water insoluble rosin resin present is up to about 45 wt.%.
5. The composition of claim 1 wherein the water insoluble rosin resin is a mixture of a low acid number rosin resin and a high acid number rosin resin.
6. The composition of claim 5 wherein the low acid number rosin resin has an acid number of up to 45.
7. The composition of claim 5 wherein the high acid number rosin resin has an acid number from about 45 to about 400.
8. The composition of claim 1 wherein the water insoluble rosin resin is selected from the group consisting of phenolic, maleic, fumaric, pentaerythritol, hydrocarbon rosin resins and mixtures thereof.
9. The composition of claim 1 wherein the water insoluble rosin resin is selected from the group consisting of dimerized and polymerized rosins, terpenes, polyamides, rosin resins, rosin salts, tall oil resins, methacrylic resins, styrene-acrylic resins, polystyrenesulfonic acid and its salts, and acrylic or vinyl emulsion

- 5 polymers prepared from monomers selected from the group consisting of acrylic acid esters, fatty acid esters, methacrylic acid esters, acrylic acid esters of polyhydric alcohols, methyl methacrylate, styrene, vinyl styrene, and vinyl acetate rosin reins, and mixtures thereof.
- 10 10. The composition of claim 1 wherein the amount of oil mixture is up to about 70 wt.%.
11. The composition of claim 1 wherein the amount of oil mixture is up to about 55 wt.%.
- 15 12. The composition of claim 1 wherein the amount of oil mixture is about 15 wt.% to about 45 wt.%.
13. The composition of claim 1 wherein the water reducible and non-
20 water reducible oils of the oil mixture are selected from the group consisting of polyester, alkyd, polyolefin and epoxy ester based oils.
14. The composition of claim 1 wherein the water reducible and non-
water reducible oils of the oil mixture is selected from the group consisting of
25 vegetable oils and fatty acid ester oils.
15. The composition of claim 14 wherein the vegetable oils are selected from the group consisting of rapseed, linseed, soybean, castor, dehydrated castor, corn, tung, otticita, carnuba, and coconut oils and mixtures thereof.
- 30 16. The composition of claim 14 wherein the fatty acid ester oils are selected from monoesters alcohols of fatty acids.
17. The composition of claim 15 further comprising a glycol or glycol ether to modify the vegetable oil.
- 35 18. The composition of claim 15 further comprising a polyglycol or polyglycol ether to modify the vegetable oil.

- 5 19. The composition of claim 1 wherein the pigment and water insoluble rosin resin are present in a parts ratio of about 1:8 to about 1:1.
20. The composition of claim 1 wherein the pigment and water insoluble rosin resin are present in a parts ratio of about 1:4 to about 1:1.
- 10 21. The composition of claim 1 wherein the amount of pH neutralizing agent is up to about 10 wt.%.
23. The composition of claim 1 wherein the amount of pH neutralizing agent is up to about 5 wt.%.
- 15 24. The composition of claim 1 wherein the pH neutralizing agent is an acid neutralizing agent.
25. The composition of claim 1 wherein the pH neutralizing agent is
20 selected from the group consisting of primary amines, secondary amines and tertiary amines.
26. The composition of claim 1 wherein the neutralizing agent is selected from the group consisting of monoethanolamine, diethanolamine,
25 dimethylethanolamine, methyldiethanolamine, triethanolamine, N-dimethylhexylamine, polyethylene imine, triethylanolamine, propylene dimaine, hexamethylene amine, urea, dibutyl amine, diethylene triamine, and mixtures thereof.
- 30 27. The composition of claim 1 further comprising water.
28. The composition of claim 27 wherein the amount of water present is up to about 25 wt.%.
- 35 29. The composition of claim 27 wherein the amount of water present is up to about 10 wt.%.
30. The composition of claim 27 wherein the amount of water present is up to about 5 wt.%.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 02/35912

A. CLASSIFICATION OF SUBJECT MATTER

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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 965 633 A (REVOL MICHEL PAUL GILLES) 12 October 1999 (1999-10-12) column 1, line 35-43 column 4, line 54-65 examples 1-28	1-16, 19, 20
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Inte of Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

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Revised by
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photolysis. Decomposition of a compound into simpler units as a result of absorbing one or more quanta of radiation; examples are splitting of hydrogen iodide by the reaction $2\text{HI} + h\nu \rightarrow \text{H}_2 + \text{I}_2$; and of ketene ($\text{H}_2\text{C}=\text{CO}$) into CO and carbene (methylene) ($=\text{CH}_2$). Photodecomposition may also occur with aldehydes, ketones, azo compounds, and organometallic compounds. Continuous generation of hydrogen by photolysis of water has been achieved using platinum catalyst in conjunction with ruthenium and rhodium. Similarly, hydrogen can be split from H_2S by photolysis with cadmium sulfide as catalyst, aided by ruthenium dioxide.

See flash photolysis; photochemistry.

photometric analysis. Chemical analysis by means of absorption or emission of radiation, primarily in the near UV, visible, and infrared portions of the electromagnetic spectrum. It includes such techniques as spectrophotometry, spectrochemical analysis, Raman spectroscopy, colorimetry, and fluorescence measurements.

See spectroscopy.

photon. The unit (quantum) of electromagnetic radiation. Light waves, γ rays, X rays, etc. consist of photons. Photons are discrete concentrations of energy that seem to have no rest mass and move at the speed of light. Their nature can be described only in mathematical terms. Photons are emitted when electrons move from one energy state to another, as in an excited atom.

See radiation.

photophor. See calcium phosphide.

photopolymer. A polymer or plastic so made that it undergoes a change on exposure to light. Such materials can be used for printing and lithography plates, photographic prints, and microfilm copying. The light may cause further polymerization or cross-linking, or it may cause degradation. One application involves the use of esters of polyvinyl alcohol that cross-link and so become insoluble, whereas unexposed portions of the material remain soluble.

photosensitive glass. Certain clear silicate glass containing ingredients capable of forming permanent photographic images when subjected to action of X rays or ultraviolet light and subsequent heat treatment.

photosynthesis. The utilization of sunlight by plants and bacteria to convert two inorganic substances (carbon dioxide and water) into carbohydrates. Chlorophyll acts as the energy converter in this reaction, which is perhaps the most important on earth. The generalized reaction is $6\text{CO}_2 + 6\text{H}_2\text{O} + 672 \text{ kcal} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$. The significance

of this process lies in the conversion of energy from radiant to chemical form. The chemical energy that a green plant stores by photosynthesis provides the total energy requirement of the plant. Directly or indirectly plants supply the primary organic nutrient for most other living organisms. Most fossil fuels are storehouses of the radiant energy transformed by photosynthesis in earlier geologic eras.

Photosynthesis is the principal source of atmospheric oxygen. At least two-thirds of the total photosynthetic activity of the earth takes place in the oceans. Its exact chemical mechanism is extremely complex. Essential features are the reduction of carbon dioxide and the utilization of the hydrogen of water to form carbohydrates, with oxygen being liberated; the nucleotides nicotinamide and adenosine triphosphate are involved in this conversion. Sugar (sucrose) is formed in the cytoplasm surrounding the chloroplasts. Photosynthesis has been shown to be substantially inhibited by air pollution to the extent of 20% in rural locations and 33% in urban areas.

See algae.

photovoltaic cell. See solar cell.

phthalamide.

CAS: 88-96-0. $\text{C}_6\text{H}_4(\text{CONH}_2)_2$. The double acid amide of phthalic acid.

Properties: Colorless crystals. Mp 220C (decomposes into phthalimide and ammonia). Very slightly soluble in water and alcohol, insoluble in ether.

Derivation: By stirring phthalamide with cold concentrated ammonia solution; by the reaction of phthalyl chloride and ammonia; or from the addition of ammonia to phthalic anhydride under pressure.

Use: Intermediate in organic synthesis, laboratory reagent.

phthalic acid. (*o*-phthalic acid; *o*-benzene dicarboxylic acid).

CAS: 88-99-3. $\text{C}_6\text{H}_4(\text{COOH})_2$.

Properties: Colorless crystals. D 1.585, mp decomposes at 191C. Soluble in alcohol; sparingly soluble in water and ether.

Derivation: Catalytic oxidation of *o*-toluic acid and oxidation of xylene.

Grade: Technical, reagent.

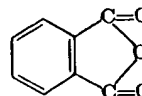
Use: Dyes, phenolphthalein, phthalimide, anthranilic acid, synthetic perfumes, laboratory reagent.

***p*-phthalic acid.**

See terephthalic acid.

phthalic anhydride.

CAS: 85-44-9. $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$.



Properties: White, crystalline needles; mild odor. Sublimes below boiling point; d 1.527 (4C), mp 131.16C, bp 285C, flash p 305F (151.6C) (CC), autoign temp 1083F (583C). Soluble in alcohol, carbon disulfide, and hot water. Combustible.

Derivation: Catalytic oxidation of naphthalene.

Method of purification: Sublimation.

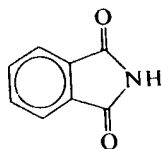
Grade: Pure, technical.

Hazard: Skin irritant. TLV: 1 ppm in air.

Use: Alkyd resins, plasticizers, hardener for resins, polyesters, synthesis of phenolphthalein and other phthaleins, many other dyes, chlorinated products, pharmaceutical intermediates, insecticides, diethyl phthalate, dimethyl phthalate, laboratory reagent.

phthalimide.

CAS: 85-41-6. $C_6H_4(CO)_2NH$.

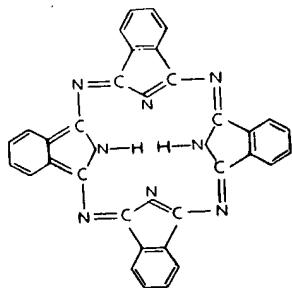


Properties: White, crystalline leaflets. Mp 233–238C, bp (sublimes). Slightly soluble in water; insoluble in benzene; soluble in boiling alcohol or acetic acid and in aqueous alkalis. Combustible.

Derivation: By dissolving phthalic anhydride in ammonium hydroxide, evaporating to dryness, and using the residue.

Use: Synthetic indigo via anthranilic acid, fungicide, organic synthesis, laboratory reagent.

phthalocyanine. Any of a group of benzoporphyrins that have strong pigmenting power, forming a family of dyes. The basic structure of the molecule comprises four isoindole groups, $(C_6H_4)_2N_4$, joined by four nitrogen atoms. Four commercially important modifications are (1) metal-free phthalocyanine, $(C_6H_4C_2N)_4$, having a blue-green color (structure shown below):



(2) copper phthalocyanine, in which a copper atom is held by secondary valences of the isoindole nitrogen atoms (see Pigment Blue 15); (3) chlorinated copper phthalocyanine, green, in which 15–16 hydrogen atoms are replaced by chlorine (see Pigment

Green 7); and (4) sulfonated copper phthalocyanine, water soluble, green, in which two hydrogen atoms are replaced by HSO_3 groups.

Use: Decorative enamels, automotive finishes, and similar applications where lightfastness and chemical stability are required.

m-phthalodinitrile. (isophthalodinitrile; IPM; *m*-dicyanobenzene; 1,3-dicyanobenzene; 1,3-benzenedicarbonitrile).

CAS: 626-17-5. $C_6H_4N_2$.

Properties: Needles. Mw 128.14, mp 141C, bp sublimes. Slightly soluble in water; insoluble in ether, acetone, hot ligroin, very soluble in alc, benzene, and chloroform.

Hazard: TLV: 5 mg/m³.

Use: Intermediate.

phthalonitrile. (*o*-dicyanobenzene).

CAS: 91-15-6. $C_6H_4(CN)_2$.

Properties: Buff-colored crystals. Mp 138C. Insoluble in water; soluble in acetone and benzene. Combustible.

Derivation: Vapor-phase reaction of ammonia and phthalic anhydride over alumina catalyst at high temperature.

Hazard: Toxic by ingestion.

Use: Intermediate in organic synthesis (especially pigments and dyes), base material for high-temperature lubricants and coatings, insecticide.

phthaloyl chloride. (phthaloyl dichloride; phthalyl chloride). $C_6H_4(COCl)_2$.

Properties: Colorless, oily liquid. Mp 16C, bp 277C, refr index 1.568 (20C). Decomposed by water or alcohol; soluble in ether. Combustible.

Derivation: By the action of phosphorus pentachloride on phthalic anhydride.

Hazard: Irritating by inhalation and skin contact.

Use: Chemical intermediate, especially for plasticizers and resins; laboratory reagent.

See isophthaloyl chloride.

phycocolloid. One of several carbohydrate polymers (polysaccharides) occurring in algae (seaweed). They are hydrophilic colloids having a tendency to absorb water, with swelling, and to form gels of varying strength and consistency. The chief types of phycocolloid are carrageenan from Irish moss, algin from brown algae, and agar from red algae. They contain complex galactose and mannose sugars and are sometimes considered seaweed mucilages.

physical chemistry. Application of the concepts and laws of physics to chemical phenomena in order to describe in quantitative (mathematical) terms a vast amount of empirical (observational) information. A selection of only the most important concepts of physical chemistry would include the electron wave equation and the quantum mechanical interpretation of atomic and molecular structure,

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